"Studies on Cr (VI) complexes as brominating agents-a kinetic and mechanistic approach"

SHORT RESUME OF THE PLAN PROPOSED FOR INVESTIGATION FOR Ph. D. DEGREE UNDER THE FACULTY OF SCIENCE.

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SWAMI RAMANAND TEERTH MARATHWADA UNIVERSITY, NANDED

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Introduction:

The study of oxidation of organic compounds is of immense importance both from mechanistic and synthetic points of view. Hexavalent chromium compounds are highly valuable oxidants for the oxidation of organic and inorganic substrates. Many reviews and books are available which have dealt at lengths with the mode of action of Cr(VI) reagents[1-12].

The earlier known Cr(VI) oxidants such as chromium trioxide,chromyl chloride, Jones reagent *etc*. lacked mildness, operationalsimplicity, versatility and selectivity which are important prerequisites for an oxidant to be useful. This consideration has led to development of new Cr(VI) based reagents and associated methodologies. Consequently various Cr(VI) reagents,with ligands such as pyridine[13-16], quinoline[17-22] and 2,2'-bipyridine[23], 4-(dimethylamino)-pyridine[24], 1-methyl imidazole[25], isoquinoline[26], imidazole [27-29], γ-picoline[30], pyrazine[31],3-carboxy-pyridine[32], benzimidazole[33] *etc*. have been developed. Among these Cr(VI) reagents pyridinium and quinolinium halochromates have been reported to be stable reagents. These reagents have been used as mild and selective oxidants in synthetic organic chemistry. Sufficient contributions have been made up-to now in the kinetics and mechanism of oxidation of organic substrates by pyridinium and quinolinium halochromates. This article presents the contribution on the oxidation reactions of organic substrates and pyridinium and quinolinium halochromates with emphasis on kinetics and mechanism.

Cr(V) complexes have been shown to undergo a variety of reactions including geometric isomerism, coordination number changes, solvation, ligand exchange and dimerisation. Normally these reactions are rapid compared to the subsequent reduction of Cr(V) by organic substrates, or disproportionation of

Cr(V) to Cr(VI) and Cr(III). Many of these rapid pre-equilibrium processes that precede the redox chemistry have been overlooked previously in developing mechanistic schemes for Cr(VI) and Cr(V) oxidations of organic and inorganic substrates. As outlined here, this will require a reinterpretation of much of the published mechanistic details on Cr(VI) and Cr(V) redox reactions. The new results also have substantial implications for understanding possible mechanisms of Cr(VI)-induced cancers, and controlling the selectivity of Cr(VI) oxidations of organic substrates.

Taking in to account all these literature survey it is found that less amount of work has been done on kinetics and mechanism of brominations by Cr(VI) complexes.hence we propose to work on a synthesis, characterization of some newCr(VI) complexes as brominating agents which may be mild,specific and selective for aromatic compounds.

a) International Status:

Pyridinium bromo chromates is a mild and selective oxidizing agent in synthetic organic chemistry. It is used in a marine paints.

b) National Status :

Recently the Indian researchers attention is drawn towards this field. considerable work is carried out in this area.

The new reagent, quinolinium bromochromate (QBC), apart from being efficient as an oxidant for alcohols, also functions as a good brominating agent for aromatic compounds.

Aims & Objectives:

1) Synthesis of different new Cr(VI) complexes and their spectral analysis.

2) Study on thermodyanamic parameters.

3) A kinetic and mechanistic study of bromination of aromatic compounds by Cr(VI) complexes.

4) Isolation of the product.

Methodology : Some new Cr(VI) complexes will be prepared by reported methods and kinetics and mechanistic study of some substituted aromatic compounds will be studied as usual.

Year wise plane of work & target to be achieved.

The proposed project work requires a period of at least three years

Year wise distribution of work

i) First year :

Review of literature & preparation of complexes and their spectral analysis.

ii) Second Year :

A kinetic study.

iii) Third Year :

A mechanistic study.

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To,

The Director,

BCUD,

SRTM University Nanded.

Sub : Submission of my Synopsis

Ref : PG/Allocation / 2016-17 dated 13.05.2017

Through : Dr. Patwari S.B. Professor, LBS college Dharmabad

Respected Sir,

With reference to the above cited subject I am here by submitting the synopsis of my research topic with consent from my allocated Research supervisor Dr. Patwari S.B. Professor Dept. of Chemistry, LBS college Dharmabad . Nanded for further action.

So kindly accept the same and oblige.

Your's faithfully

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